UNCLASSIFIED

Defense Technical Information Center
Compilation Part Notice

ADP014326

TITLE: Observation of the Verwey Transition in Fe3O4 Nanocrystals

DISTRIBUTION: Approved for public release, distribution unlimited

This paper is part of the following report:

TITLE: Materials Research Society Symposium Proceedings. Volume 746. Magnetoelectronics and Magnetic Materials - Novel Phenomena and Advanced Characterization

To order the complete compilation report, use: ADA418228

The component part is provided here to allow users access to individually authored sections of proceedings, annals, symposia, etc. However, the component should be considered within the context of the overall compilation report and not as a stand-alone technical report.

The following component part numbers comprise the compilation report:
ADP014306 thru ADP014341

UNCLASSIFIED

Mat. Res. Soc. Symp. Proc. Vol. 746 © 2003 Materials Research Society Q4.1

Observation of the Verwey Transition in Fe_3O_4 Nanocrystals

Gil Markovich[1], Tcipi Fried[1], Pankaj Poddar[1], Amos Sharoni[2], David Katz[2], Tommer Wizansky[2], and Oded Millo[2]
[1]School of Chemistry, Tel Aviv University, Tel Aviv 69978, Israel
[2]Racah Institute of Physics and the Center for Nanoscience and Nanotechnology, The Hebrew University of Jerusalem, Jerusalem 91904, Israel

ABSTRACT

The electronic properties of arrays and isolated magnetite nanocrystals were studied using tunneling spectroscopy. Macroscopic tunnel junctions were used to study stacked arrays of the nanocrystals. The temperature dependent resistance measurements showed an abrupt increase of the resistance around 100 K, attributed to the Verwey metal-insulator transition, while the current-voltage characteristics exhibit a sharp transition from an insulator gap to a peak in the density of states near the Fermi energy. This conductance peak was sensitive to in-plane magnetic field showing large magnetoresistance. The tunneling spectra obtained on isolated particles using a Scanning Tunneling Microscope exhibit a gap-like structure below the transition temperature that gradually disappeared with increasing temperature, ending with a small peak structure around zero bias.

INTRODUCTION

The Verwey metal-insulator transition observed in magnetite (Fe_3O_4) has continuously attracted interest since its discovery more than 60 years ago[1]. Magnetite is a relatively good conductor at room temperature and on cooling below 120K its conductivity sharply drops by two orders of magnitude. It was described as a first-order metal-insulator transition accompanied by a structural phase transition where the cubic symmetry of the Fe_3O_4 crystal is broken by a small lattice distortion [2]. While the exact nature of the transition is still under controversy, it is understood that the driving force for this phenomenon is the strong electron-electron and electron-lattice interactions in the system.

Special attention has been focused on the roles played by long-range and short-range charge ordering in driving the Verwey transition. The former is believed to exist below the transition temperature, T_V, and the latter sustains well above it. The long-range order manifests itself by opening a gap in the electronic density of states (DOS) around the Fermi level (E_F). This gap was detected by photoemission [3,4], optical [5], and tunneling [6] spectroscopies. The effect of short-range ordering on the DOS is not as clear. However, recent photoemission experiments [3,4] suggest that a reduced gap in the DOS, associated with a short-range ordering, still exists well above the transition temperature.

In view of the importance of long-range charge ordering in determining the electronic properties below T_v, an intriguing question arises: Could the Verwey transition be observed in nanoscale magnetite crystals of diameter measuring several unit cells? Recently, Poddar et al. reported on the observation of a sharp Verwey transition in arrays of Fe_3O_4 (magnetite) nanoparticles of average size around 5.5 nm. This transition was manifested both in a resistance jump as well as in a change in the tunneling spectra measured on the arrays. However, it was not clear whether the observed transition pertained to the single nanocrystal (NC) or was a collective

array effect. In this paper we present scanning tunneling spectroscopy results on single nanoparticles, providing evidence that the transition occurs in isolated magnetite NCs. The tunneling spectra show a gap structure in the DOS below T_v, which gradually transforms into a peak around E_F.

EXPERIMENTAL DETAILS

The details of magnetite NCs array preparation are described elsewhere [7]. After synthesis, the NCs were coated with oleic acid, dispersed in non-polar organic solvents and separated by employing size selective precipitation to produce uniform samples of NCs in the 3-10 nm size range. Transmission electron microscopy (TEM) was used for size determination as well as to confirm the formation of NC monolayers. The monolayers were produced by depositing the hydrophobic magnetite nanocrystals from heptane solution at the air-water interface and compressing the film two-dimensionally to form a close-packed array. For the fabrication of the junctions, arrays of gold lines (width = 80μm) and a thickness of 100 nm were deposited on a doped Si substrate with a 100 Å thick oxide layer. Consequently, five monolayers of Fe_3O_4 NCs were transferred from the air-water interface onto the patterned substrates using the Langmuir-Schafer technique. A second array of gold lines perpendicular to the bottom electrodes was deposited by thermal evaporation through a shadow mask on top of the films while the substrate was maintained at 20 °C. The electrical contacts were formed by fixing Cu wires to pads on the gold electrodes using silver paste [8].

For the scanning tunneling microscopy (STM) measurements, the magnetite particles were spin-coated on gold films deposited on mica substrates and then dipped in oleic acid solution. The fatty acid molecules served as a protecting layer against NC oxidation. All this procedure was performed in an inert atmosphere. The low temperature tunneling spectra were obtained using the double barrier tunnel junction configuration, by positioning the STM tip above single NCs [9,10]. The tip was retracted as far as possible from the NC in order to form a highly asymmetric tunneling configuration and thus reduce single electron charging effects [10,11]. This was facilitated by the preparation procedure that ensured a relatively large capacitance and small resistance (large tunneling rate) for the substrate-NC tunnel junction. Nevertheless, many NCs did show charging effects that dominated the tunneling characteristics, thus masking the intrinsic NC density of states, and only about ten NCs could be used for studying the temperature dependence of the DOS around T_v.

RESULTS AND DISCUSSION

The temperature dependence of the two-terminal resistance of a macroscopic tunnel junction is shown in Figure 1a. The sharp resistance jump observed at 100±5 K clearly manifests the first-order Verwey transition. The typical transition temperature measured for the arrays is smaller than T_v observed for high-quality bulk samples (~120 K). This may be due to either surface or finite size effects. This temperature is independent of the bias voltage used in the measurement but magnitude of the resistance jump decreases with increasing bias due to non-linearity. In Figure 1b we present dI/dV vs. V tunneling spectra measured above and below T_v, both with and without applying an in-plane magnetic field. Two significant effects can be observed in these data: 1. A pronounced change in the tunneling conductance curve takes place on cooling through T_v. The sharp peak around zero bias (E_F) seen right above T_v disappears abruptly, and a region of

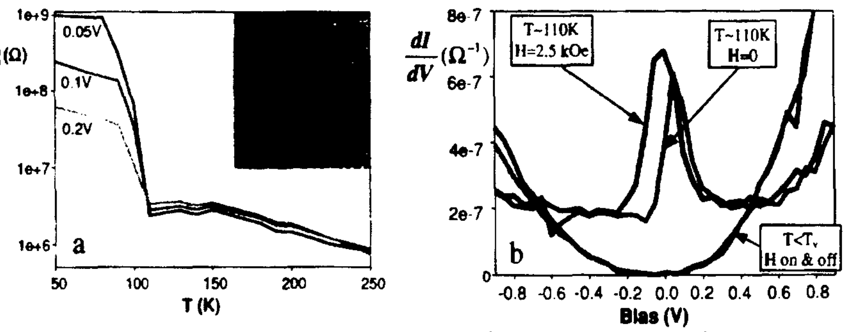

Figure 1. (a) Magnetite nanocrystal film resistance as function of temperature for three bias voltage values. Inset: TEM image of a magnetite NC monolayer with average particle size of 5.5 nm. (b) Differential conductance vs. bias voltage above and below the transition temperature, with (black lines) and without (gray lines) in-plane magnetic field of 2.5 kOe.

low conductance sets-in instead below T_v. 2. Upon application of an external magnetic field the conductance peak broadens and shifts to negative bias, resulting in a large negative magnetoresistance around zero bias. These effects were reversible and reproducible through several cooling-heating cycles [8].

The macroscopic tunnel junctions are perceived as consisting of parallel percolating current paths, where each path may include several inter-particle junctions. Hence, the details of the current-voltage curves are determined not only by the single-particle electronic structure but also by the *RC* constants of the various inter-particle tunneling junctions along the current paths. However, since the *RC* characteristics of the junctions are not sensitive to temperature, we believe that the abrupt change in the tunneling spectra is a manifestation of the MI transition in the single particle. In particular, it appears that in the metallic phase (above 100 K), the conductance peak near the Fermi level reflects the narrow conduction band of magnetite, as previously observed on bulk samples [12]. Below T_v the region of low conductance around zero bias results from opening a gap in the DOS around E_F of the NCs, but its width is determined by the inter-particle junction parameters. Tunneling spectroscopy measurements on single particles, as enabled by STM, may yield further information on the evolution of the gap in single NCs around T_v, as will be discussed below.

External magnetic field affects the electron transport in the arrays by aligning the magnetic moments of the individual superparamagnetic NCs along the conduction paths. As the magnetizations of the particles become aligned with the external field, their spin polarized conduction bands, located near E_F, align respectively, and the probability for electron tunneling through a chain of particles increases. This leads to a negative magnetoresistance behavior, as depicted in Fig. 1(b). The magnetic field influence on the tunneling spectra was found to decrease upon heating the samples to room temperature [8]. This effect is due to thermal agitation that disturbs the relative magnetization alignment between neighboring particles, consequently reducing the magnetoresistance. Increasing the temperature could also reduce the degree of spin polarization within individual particles, further contributing to the reduction in the magnetoresistance.

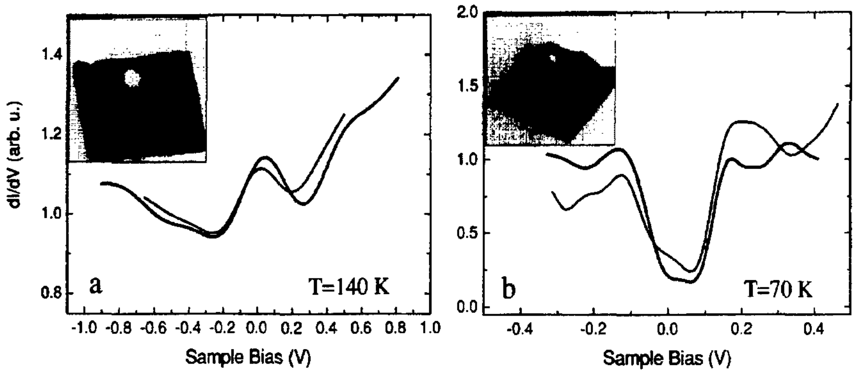

Figure 2. Tunneling spectra taken on isolated magnetite NCs above (a) and below (b) the Verwey transition temperature. The two curves in each frame were taken over the same NC with the same conditions, showing the variance in the data. The insets present STM images of the corresponding NCs (image sizes are: (a) 26x30 nm, (b) 52x40 nm).

Turning now to the STM results, we present in Fig. 2 tunneling spectra measured on single magnetite NCs, about 8 nm in diameter. The curves in Fig. 2(a) were measured at 140 K, well above T_v, whereas those in Fig. 2(b) were acquired at 70 K. Consistent with the macroscopic tunnel junction measurements, a peak in the DOS is observed above the Verwey transition while a gap develops below the transition. The reproducibility of the data can be appreciated from two typical curves plotted for each particle: the main features, namely, the peak and gap structures, are reproducible, but the background may fluctuate. Due to drift of the STM tip upon changing the temperature, we were not able to measure, in most cases, the same NC well above and well below T_v. The measured gap value in Fig. 2(b) is about 250 meV, which is significantly larger than previously measured on bulk samples using photoemission (~ 140 meV) [3,4] or STM (200 meV) [6]. This apparent gap broadening may be due to the effect of voltage division, inherent to the double barrier tunnel junction configuration [10,11]. We have observed a clear gap structure below T_v in about half of the measured nanoparticles that did not exhibit single electron charging effects, where the gap values varied between 250 to 350 meV. The peak width was typically 400 meV, somewhat larger than the value obtained using the macroscopic tunnel junction, ~ 300 meV (see Fig. 1).

Figure 3 depicts the evolution of the DOS around E_F with temperature. Here, the tunneling spectra were acquired on a small cluster of (single layer) NCs, nominally at the position marked by the white arrow. One can see that as the temperature is increased, the gap reduces, and the DOS at the Fermi energy gradually increases. The two spectra at 105 K may have been obtained (due to drift of the tip) at somewhat different positions, resulting in a different tunneling DOS. In these measurements it appears that a clear gap still exists even above 100 K (the transition temperature measured for the NC arrays) and the peak structure emerges only at a higher temperature, in contrast to the more abrupt change observed for the arrays, as discussed above. This may reflect the particle-to-particle fluctuations (e.g., in composition or surface condition), to which the STM is sensitive, as opposed to the macroscopic tunnel junction where the ensemble properties are measured. In this context we note that some of the NCs did not exhibit in our STM spectra any transition behavior whatsoever. Interestingly, the suppression of the gap

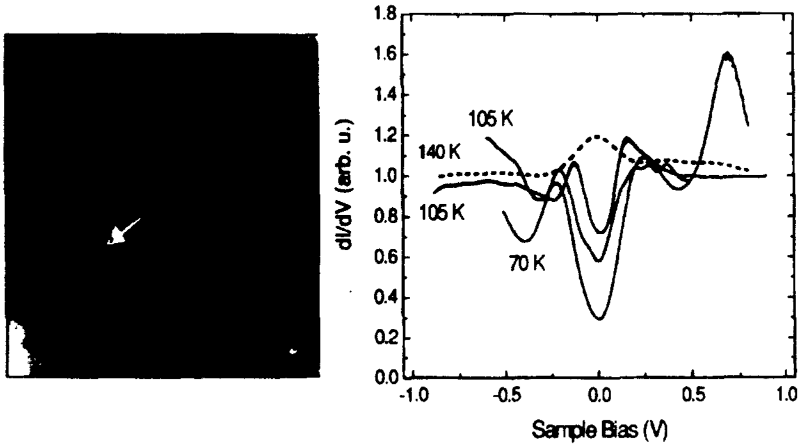

Figure 3. 20x20 nm^2 STM image showing a cluster of magnetite NCs (left) together with a series of tunneling spectra taken nominally at the position marked by the arrow at various temperatures, as indicated (right).

in the Fe_3O_4 NCs around T_v, as observed in both types of our tunneling experiments, is faster than that seen for bulk samples using photoemission and optical spectroscopies [3,4,5]. As the gap in the DOS above T_v was attributed to the short-range charge ordering, it is expected that this gap would exist also in the nanocrystals, and it is therefore puzzling why it was not detected in the tunneling spectra.

CONCLUSIONS

The combination of macroscopic tunnel junctions and scanning tunneling spectroscopy is demonstrated to be an effective tool for studying the electronic properties of Fe_3O_4 NC in the vicinity of the Verwey transition. In particular, the STM measurements clearly show that the sharp resistive transition observed for NC arrays is associated with, and probably governed by, an opening of a gap in the electronic DOS around E_F in single NCs. This result suggests that long-range order, that is believed to dominate the electronic properties at $T<T_V$, is significant even in nanometer size magnetite particles. More detailed size dependent experiments are still needed to resolve the finite size effects on the transition temperature and the electronic structure of the magnetite system. Understanding these issues as well as the magnetoresistance properties of the magnetite NC arrays may lead to its exploitation as a novel material for spin polarized nanodevices.

ACKNOWLEDGEMENTS

This work was supported in parts by the Israel Science Foundation, The Israel Ministry of Science and the DIP Foundation.

REFERENCES

1. E. J. W.Verwey, Nature **144**, 327 (1939).
2. M. Izumi, T. F. Koetzle, G. Shirane, S. Chikazumi, M. Matsui, and S. Todo, *Acta Crystallogr., Sect. B: Struc. Sci.* **38**, 2121 (1982).
3. J.H. Park, L.H. Tjeng, J.W. Allen, P. Metcalf, and C.T. Chen, *Phys. Rev. B* **55**, 12813 (1997).
4. A. Chainani, t. Yokaya, T. morimoto, T. Takahashi, and S. Todo, *Phys. Rev. B* **55**, 17796 (1995).
5 L.V. Gasparov, D.B. Tanner, D. B. Romero, H. Berger, G. Margariotondo, and L. Forro, *Phys. Rev. B* **62**, 7939 (2000).
6. J.Y.W. Wei, N.C. Yeh, R.P. Vasquez, and A. Gupta, *J. Appl. Phys.* **83**, 7366 (1998).
7. T. Fried, G. Shemer, and G. Markovich, *Adv. Mater.* **13**, 1158 (2001).
8. P. Poddar, T. Fried, and G. Markovich, *Phys. Rev. B* **65**, 172405 (2002).
9. A.E. Hanna and M. Tinkham, *Phys. Rev. B* **44**, 5919 (1991).
10. D. Katz, O. Millo, S. H. Kan, and U. Banin, *Appl. Phys. Lett.* **79**, 117 (2001).
11. E. P. A. M. Bakkers and D. Vanmaekelbergh, *Phys. Rev. B* **62**, R7743 (2000); E. P. A. M. Bakkers, et al., *Nano Lett.* **1**, 551 (2001).
12. A.Gupta and J.Z. Sun, *J. Magn. Magn. Mater.* **200**, 24 (1999).